EFFECT OF PH ON SMECTITE DISSOLUTION RATES UNDER ALKALINE CONDITIONS

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Stirred-flow-through dissolution experiments were carried out to measure the smectite dissolution rates under alkaline conditions and to evaluate the effect of pH on the rates. The experiments were performed for mixed NaOH-NaCl aqueous solutions of initial pHs of 9.0, 10.0, 11.0, 12.0 and 13.3 with ionic strength of 0.3 M. For each of the runs, 120 mg of the purified smectite (Kunipia-P® provided from Kunimine Industry Co Ltd) was added to a cylindrical Teflon® reactor (120ml in volume), and the solution was added through Tygon® tube at a flow rate of 0.2 ml / min (10 hrs in residence time). This flow rate was low enough to prevent the outlet filter of the reactor from clogging with the smectite powder. The reactors were fully immersed in a water bath to hold at the constant temperature of $50 \pm 1°C$. The output solutions were periodically analyzed for Si, Al, and pH, and the dissolution rates were calculated from the steady-state Si concentration. The experimental procedure including preparation and stock of input solutions, and sampling of output solutions were carried out in a globe box under N_2 gas atmosphere to avoid possible effects of the atmospheric CO_2 on the solution pH. The total Al and Si concentrations were determined calorimetrically using the catechol violet method and molybdate blue method, respectively on a UV-visible spectrophotometer.

High concentrations in Si and Al were observed at the onset of all of the runs. The concentrations gradually decreased to steady state values within at least until 7 days. The pH decreased to 8.0 in the pH 9.0 run and to 9.6 in the pH 10.0 run. The decrease in pH was probably caused by the release of anionic silica and alumina species from the smectite surface. No appreciable changes in pH were observed at higher-pH runs. The XRD detected no significant change in the mineral compositions and no formation of secondary minerals such as analcime within the duration investigated. Therefore, it is reasonable to assume that the reactions proceeded in the steady state proceeded at pHs 8.0, 9.6, 11.0, 12.0, and 13.3, and that the Si concentration at the steady state should be attributed to the congruent dissolution of the starting smectite.

The dissolution rates were calculated from the Si concentrations, BET surface areas (initial surface area) and the flow rates of reaction fluid. The obtained values were $10^{-11.87}$, $10^{-10.91}$, $10^{-10.61}$, $10^{-10.38}$, $10^{-10.02}$ (mol/m²s) for pH 8.0, 9.6, 11.0, 12.0 and 13.3, respectively. The dissolution rate increased as function of the pH. The dissolution rate was found to be linearly dependent on the hydroxyl activity in solution on the pH-logarithmic rate plot. The slope for the basic region of the pH-dependent dissolution rate is 0.33. Relationship between the dissolution rate and the pH can be presented as follows.

$$\text{Rate} = 10^{-9.71} a_{OH^-}^{0.33} \ (\text{mol/m}^2\text{s}) \ \text{pH} > 8.0$$

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This equation, obtained at conditions far from the reaction equilibrium by stirred-flow-through experiments, exclusively expresses the dependence of the dissolution rate of smectite on the solution pH. The reaction order, 0.33, is similar to those obtained for dissolution of silicate minerals such as feldspars, pyroxene, and amphiboles (so called "proton-promoted dissolution). The similarity in the reaction order implies that the dissolution rate of smectite is directly proportional to the surface concentration of negative charged sites on silanol and alminol, as already pointed out by previous studies.

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